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AMS analysis of iodine-129 in aerosols from Austria

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ABSTRACT

Atmospheric concentrations of many elements have been significantly increased by human activities. The quantification of these changes and their effect on the terrestrial and aquatic ecosystems is important because of their potentially adverse effects. The human nuclear activities, especially releases from the spent nuclear fuel reprocessing plants, are presently the main source of ^{129}I in the environment.

In this work, the concentration of ^{129}I and the ratios of ^{129}I/^{127}I in aerosols weekly collected in Vienna, Austria (202 m a.s.l) during the year 2001 are presented. Iodine was extracted from the aerosol filters using a strong basic solution and separated from the matrix elements by anion exchange. The chemical yield of the procedure, determined by ICP-MS, ranges from 70% to 95%. The AMS results indicated that the ^{129}I/^{127}I isotopic ratios were of the order 10^{-8} to 10^{-7}. The ^{129}I originated from gaseous emissions from the Sellafield reprocessing plant. The measured ^{129}I concentrations were compared with those of ^{7}Be, a cosmogenic radionuclide. Although, both radionuclides exhibit nearly the same distribution pattern (higher levels in summer and lower in winter) their different origins can clearly be deduced from short term variations.

1. Introduction

The long-lived isotope of iodine ^{129}I (half-live 15.7 Ma) is introduced into the environment primarily by spontaneous fission of uranium in the earth-crust and in oceans, and by cosmic-ray induced spallation of xenon in the stratosphere leading to a natural pre-anthropogenic ^{129}I/I ratio in the order of $\sim 10^{-13}$ [1]. The military and civilian use of induced nuclear fission has increased this level by several orders of magnitude during the last 60 years. In addition, substantial emissions originate from reprocessing of spent nuclear fuel.

The interest in ^{129}I is increasing, particularly with regard to the operation of nuclear fuel reprocessing plants [2]. ^{129}I released to the atmosphere from nuclear fuel reprocessing facilities at La Hague (F) and Sellafield (UK) is assumed to have the form of CH_3I, which is relatively inert and stable (or repeatedly cycles through photolytically-formed reactive intermediates back to CH_3I). In this form, it may be transported globally in the troposphere within approximately 14 days [3–5]. In the troposphere the chemistry may involve complex cycling, which forms iodine oxides, due to photolysis and reactions with atmospheric volatile active radicals, i.e. peroxides, hydroxides, ozone, activated oxygen. The long radiological half-life of ^{129}I prevents this nuclide from disappearing, causing it to enter via precipitation or dry deposition into the environmental and geochemical cycles of stable iodine [6] although the concentration of total ^{129}I is much lower than that of the stable ^{127}I. The released ^{129}I has found wide applications in geological, environmental and oceanographic studies [7–9].

However, in spite of its environmental relevance, data on the presence of ^{129}I associated to aerosols are rather scarce. Previous studies have been carried out by neutron activation analysis (NAA) of iodine extracted from animal thyroids (sometimes in areas directly affected by gaseous emissions) to assess the increase of ^{129}I in the environment. In the case of other samples (e.g. precipitation or aerosols) accelerator mass spectrometry (AMS) was the preferred method due to its clearly lower limits of detection. AMS results for ^{129}I concentrations and ^{129}I/^{127}I isotopic ratios of air samples from Spain and Sweden have already been published. The ^{129}I concentration in aerosol particles from southern and northern Sweden ranged during the period 1983–2008 between (0.4–40.4) and (0.07–8.9) $\times 10^5$ atoms m^{-3}.

In Seville, Spain the ^{129}I concentration in aerosols varied between (0.13–1.93) $\times 10^5$ atoms m^{-3} for the year 2001. On the other hand, the concentration of the ^{129}I in gaseous form during 1993–1994 and 1998, (4.3–15.6) $\times 10^5$ atoms m^{-3} and (3.3–22) $\times 10^5$ atoms m^{-3}, respectively, was clearly higher than in aerosol particles [10–13].

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In this paper, we report on ^{129}I concentrations and ^{129}I/^{127}I isotopic ratios in aerosols sampled in Vienna, Austria during the year 2001. Iodine isotopes were determined by ICP-MS and AMS after aqueous extraction. Our main goal in the present study was to present data from a continental site, to identify the annual variability of ^{129}I in the atmosphere and to evaluate the impact of the gaseous emission from Sellafield (and to a minor extent from La Hague). A few weeks after sampling, the air filters were first measured γ-spectrometrically to determine ^{7}Be concentrations before starting the iodine analysis. Beryllium-7 is a short-lived ($t_{1/2}$ 53.2 days), cosmogenically produced radionuclide that rapidly associates with atmospheric aerosols and deposits on the Earth's surface primarily via precipitation, but also via dry deposition. It might be interesting to compare the temporal variations of an anthropogenic and a cosmogenic radionuclide.

2. Experimental

During the year 2001, air sampling was performed weekly at the meteorological station in Vienna (Hohe Warte 48°15′N and 16°21′50″E; 202 m a.s.l) 1.2 m above ground level with a flow rate of around 80 m^3/hour air using 20.3 × 25.4 cm^2 glass microfiber filters. Two filters, each of them representing a week's sampling, were combined to get biweekly samples so all measurements could be done in duplicates for accuracy and precision.

In order to extract ^{129}I, the separation method available in the literature was slightly modified [12–17]. We have developed a purification method using an ion-exchange column avoiding in this way the toxic CCl_4. Fig. 1 shows the chemical procedure for the separation of iodine from aerosols. The filters were immersed in 100 mL of extracting solution containing 0.5 M NaOH and 0.05 M $NaHSO_3$, put in ultrasonic bath for 15 min and stirred overnight. The mixture was boiled with stirring under reflux for one and half hour then cooled and filtered through 0.45 μm filter paper. This step was used in order to decompose potential organics and to release iodine into the solution as inorganic iodine. After collection of an aliquot of the solution to quantify the stable iodine concentration in air by ICP-MS [18], 1 mL of iodide carrier was added (c = 5 mg/mL I^-). The solution was loaded onto the column packed with already conditioned 10 g of Dowex 1 × 8 (100–200 mesh Cl^- form) and was washed with 50 mL 0.1 M HNO_3. Iodide was eluted with 200 mL of 0.5 M HNO_3. An aliquot of solution was taken for chemical yield determination (by ICP-MS). The chemical yield in this procedure ranged from 70% to 95%. Subsequently, iodine was precipitated as AgI by addition of 4 mL of 0.01 M $AgNO_3$. Silver iodide was thereafter isolated by centrifugation. The precipitates were washed with 25% NH_3 and twice with Millipore water in order to dissolve other halides that may have precipitated with AgI. Finally, the dried precipitates were mixed with silver powder (AgI:Ag 1:1 by weight) and pressed into copper targets for AMS measurement. The contamination introduced in the process was determined by the preparation of blank samples processed in the same way as real samples.

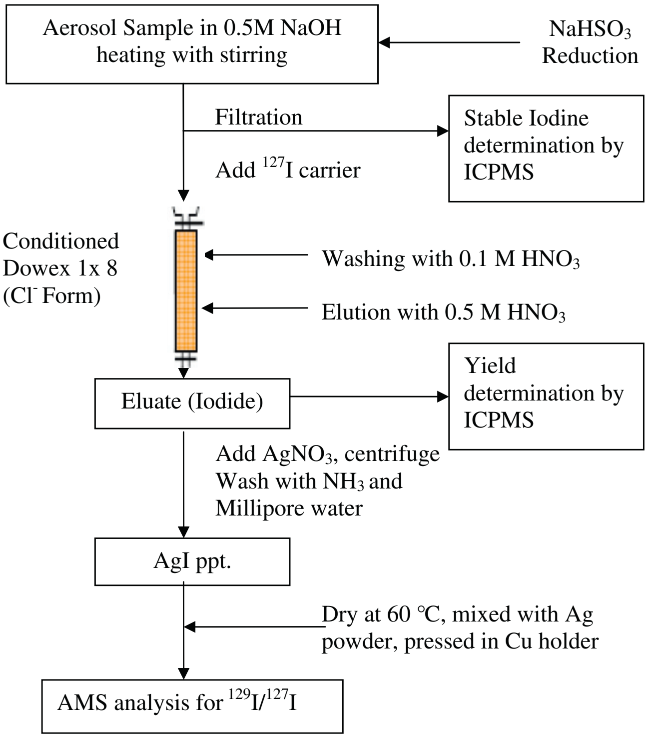

Fig. 1. Chemical procedure for the separation of iodine from aerosols.

The extraction of iodine from aerosols was also investigated as a function of leaching time. For this purpose, an air filter was divided into four parts which were leached for 1.5, 3, 4.5 and 6 h, respectively. The content of iodine in each sample was determined by ICP-MS after filtration. The samples had an average ^{127}I concentration of 14.3 ppb with a relative standard deviation of 12% without any bias.

The ^{129}I/^{127}I ratio was determined by AMS at the Vienna Environmental Research Accelerator (VERA) using 3 MV terminal voltage for the selection of charge state +4. Ratios were normalized using a standard material "ETH-D2" provided by the ETH Zürich with a nominal isotopic ratio of 4.73×10^{-11}. This material was produced by dilution of the NIST reference material SRM 4949B-79 [19]. Details are given elsewhere [20]. The blank values were $<9.65 \times 10^{-13}$ and much lower of the sample ratios of $(529–7111) \times 10^{-13}$. For the measurement of stable iodine using ICP-MS, the samples were diluted with a 2% ammonia solution and Cs was used as an internal standard (ICP-MS Agilent 7500ce, Waldbronn, Germany, equipped with a CETAC ASX-520 autosampler). The blank values were $<2\ \mu g\ L^{-1}$ whereas the corresponding values for the samples varied between 4 and 22 $\mu g\ L^{-1}$. The measurement error was <5% at one standard deviation.

To elucidate atmospheric concentrations of ^{7}Be, γ-spectrometric determinations were carried out using a REGe Detector (Canberra GR 2020). The counting time of weekly collected samples was 1000 min. For the determination of the ^{7}Be concentration the photopeak at 477.6 keV was used.

3. Results and discussions

Biweekly air samples collected in Vienna, Austria during the year 2001 were prepared and analyzed by ICP-MS and AMS. The measured concentrations of ^{127}I and ^{129}I are listed in Table 1. It can be seen that the stable iodine concentration varied between 0.5 and 1.4 ng Nm^{-3} approaching the lower end of the range of 0.2–10 ng m^{-3} given in the literature [10]. This is probably related to the fact that the studied area is situated far away from the sea, the main source for iodine in air. Fig. 2 shows the correlation between total iodine concentration and the mass of the dust particles found on our filters. As one would expect there is more dust during the winter months because of heating emissions and elevated traffic. As emissions from coal and fuel combustion also contain iodine [21–23] the stable iodine generally follows this pattern.

The time sequence of ^{129}I concentration in the air shows clear fluctuations between consecutive samples. The same situation was observed in time profiles of rainwater from three sampling stations in Europe (Uppsala, Zürich and Seville) [24]. It has been shown that the iodine concentration is a time-dependent function

Table 1
Concentration of iodine isotopes and beryllium-7 in air filters.

Sample 2001	Period	^{127}I concentration (ng Nm^{-3})	^{129}I concentration (10^5 atoms Nm^{-3})	^{129}I/^{127}I ratio (10^{-8} atoms/atoms)	^{7}Be activity (mBq Nm^{-3})
January	15/1/2001–29/1/2001	1.3 ± 0.01	2.2 ± 0.05	3.5 ± 0.06	2.1 ± 0.2
	29/1/2001–12/2/2001	1.0 ± 0.01	2.9 ± 0.12	6.3 ± 0.5	2.0 ± 0.1
February	12/2/2001–26/2/2001	1.2 ± 0.01	5.6 ± 0.24	10.1 ± 0.3	2.3 ± 0.1
	26/2/2001–12/3/2001	1.0 ± 0.01	2.4 ± 0.08	5.2 ± 0.13	2.3 ± 0.1
March	12/3/2001–26/3/2001	0.9 ± 0.01	1.7 ± 0.06	4.0 ± 0.16	2.8 ± 0.2
	26/3/2001–9/4/2001	1.3 ± 0.02	2.9 ± 0.1	5.0 ± 0.13	3.1 ± 0.2
April	9/4/2001–23/4/2001	0.7 ± 0.01	3.1 ± 0.1	9.2 ± 0.4	1.6 ± 0.1
	23/4/2001–7/5/2001	1 ± 0.01	0.4 ± 0.007	0.8 ± 0.01	4.4 ± 0.3
May	7/5/2001–21/5/2001	1.0 ± 0.01	5.1 ± 0.2	10.5 ± 0.4	4.1 ± 0.2
	21/5/2001–5/6/2001	0.90 ± 0.01	9.3 ± 0.4	21.7 ± 0.7	5.3 ± 0.3
June	5/6/2001–18/6/2001	0.5 ± 0.01	3.2 ± 0.1	14.6 ± 0.9	4.0 ± 0.3
	18/6/2001–2/7/2001	0.7 ± 0.01	5.9 ± 0.3	18.8 ± 0.7	4.9 ± 0.3
July	2/7/2001–16/7/2001	0.7 ± 0.01	2.3 ± 0.08	6.7 ± 0.2	4.8 ± 0.3
	23/7/2001–30/7/2001	0.6 ± 0.01	6.8 ± 0.2	25.1 ± 1.3	3.7 ± 0.2
August	13/8/2001–27/8/2001	0.9 ± 0.01	3.3 ± 0.08	7.4 ± 0.2	5.9 ± 0.4
September	27/8/2001–10/9/2001	0.8 ± 0.01	7.6 ± 0.4	19.5 ± 0.8	2.9 ± 0.2
	10/9/2001–24/9/2001	0.6 ± 0.01	5.2 ± 0.15	18.0 ± 0.6	2.2 ± 0.1
October	24/9/2001–8/10/2001	0.8 ± 0.01	2.1 ± 0.08	5.6 ± 0.2	2.8 ± 0.2
	8/10/2001–22/10/2001	1.1 ± 0.01	0.9 ± 0.03	1.7 ± 0.05	3.4 ± 0.2
November	22/10/2001–5/11/2001	1.2 ± 0.02	2.9 ± 0.1	8.4 ± 0.13	3.2 ± 0.2
	5/11/2001–19/11/2001	1.4 ± 0.01	5.5 ± 0.2	10.3 ± 0.3	1.9 ± 0.1
December	19/11/2001–3/12/2001	1.2 ± 0.01	8.4 ± 0.2	14 ± 0.4	2.7 ± 0.2
	3/12/2001–17/12/2001	1.3 ± 0.01	5.8 ± 0.2	10.9 ± 0.3	2.0 ± 0.1

One biweekly sample of August is missing.

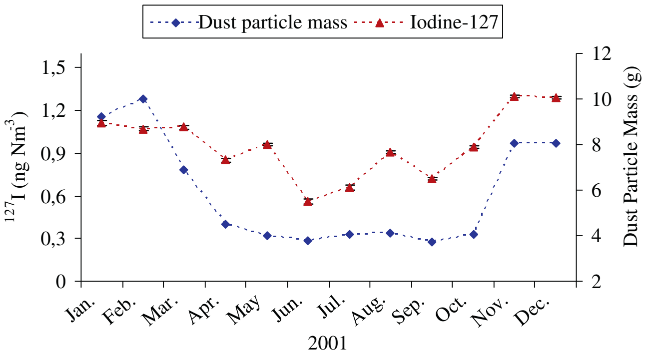

Fig. 2. Total iodine concentration and dust particle mass collected during one week.

of meteorological conditions (frequency and direction of wind, precipitation etc.), presence of dust particles in air, seasonal effects, emissions from coal combustion, soil and plants [21–23]. In spite of these different influences, we tried to find positive correlations between our data and emission data from Sellafield.

The measured data for ^{129}I concentrations show larger variations compared with those of ^{127}I. The concentration ranged between $(0.9–9.3) \times 10^5$ atoms Nm^{-3}, also consistent with those obtained by Englund [10] for southern and northern Sweden (0.4–40.4) and $(0.07–8.9) \times 10^5$ atoms m^{-3} during 1983–2008 and by Santos in Spain $(0.13–1.93) \times 10^5$ atoms m^{-3} for the year 2001 [11]. The fact that the data showed no apparent correlation between ^{127}I and ^{129}I (Fig. 3) confirmed the assumption of different dominant sources of the two isotopes: sea spray for ^{127}I and gaseous emissions from reprocessing plants (especially Sellafield) for ^{129}I. In Fig. 4 the number of ^{129}I atoms per Nm^3 of air as well as the monthly amount of gaseous ^{129}I emissions from the Sellafield reprocessing facility are given and a good correlation between these two sets of data can be seen: the main amount of ^{129}I was released between May and September 2001, when we also observed elevated concentration in Vienna. This indicates that a significant amount of discharges were transported to Austria through winds from west and north-west. This suggestion is supported by weather data: especially during the second half of May and June, and the

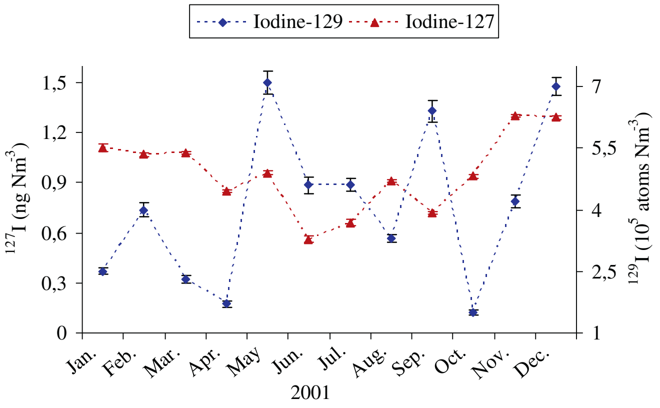

Fig. 3. Total stable iodine and ^{129}I in air samples collected in Vienna.

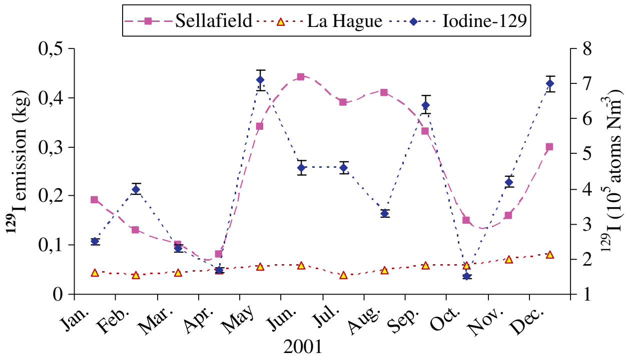

Fig. 4. ^{129}I concentration in aerosols from Vienna, Austria together with monthly gaseous emissions from the reprocessing facilities at La Hague and Sellafield.

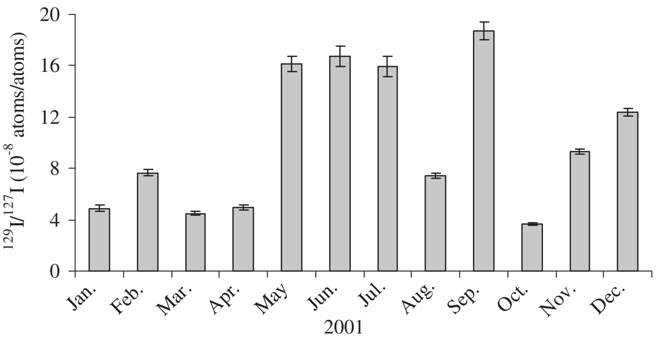

Fig. 5. Time profile of ^{129}I/^{127}I isotopic ratios.

first half of September these winds were predominant, while during July and especially during August winds from these directions were only feeble.

The temporal variations of ^{129}I/^{127}I isotopic ratios are shown in Table 1 and Fig. 5. Values span from 0.8×10^{-8} to a maximum of 25.1×10^{-8} with representative value of 10.3×10^{-8} for the year 2001 (arithmetic mean value). The highest ratios were found in summer when the stable iodine concentrations were lower and the ^{129}I values higher due to Sellafield emissions. Our values show good agreement with southern and northern Sweden (22×10^{-8} and 24×10^{-8}, respectively, as an average of the years 2001–2005) but are clearly higher than Seville, southwest of Spain (15.1×10^{-9} for the year 2001). This is plausible not only due to the larger distance of Seville from the reprocessing plant, but may also be due to the fact that the predominant winds there are from south and west, but not from north [10,11].

Fig. 6 presents the mean monthly concentration of the cosmogenic ^{7}Be and the anthropogenic ^{129}I. ^{7}Be activity data as shown in Table 1 range between (1.6–5.9) mBq m^{-3} and show the typical seasonal cycle of a middle-latitude site with maxima in spring and summer caused mainly by stratosphere-to-troposphere exchange and downward transfer [25–27]. The maximum value was measured in August when a stable high pressure system yielded hot and sunny days. Under these conditions additional ^{7}Be contributions from stratospheric or higher tropospheric levels can be expected [25]. At the end of August, this period ended with thunderstorms and also the first week of September was characterized by rain and a drop of temperature. The rainfall obviously washed out the atmospheric aerosol leading to a sharp drop in the atmospheric ^{7}Be concentration. In August and September the completely contrary "behavior" of the respective radionuclide concentrations was a consequence of their distinct sources. In the calm August we had mainly vertical air transport leading to elevated levels of ^{7}Be, while ^{129}I concentration stayed low (although there were emissions in Sellafield). In September the weather was unstable with winds bringing ^{129}I from north-west. Now horizontal mixing was clearly predominant and so the ^{7}Be concentrations dropped again to "normal" surface air levels.

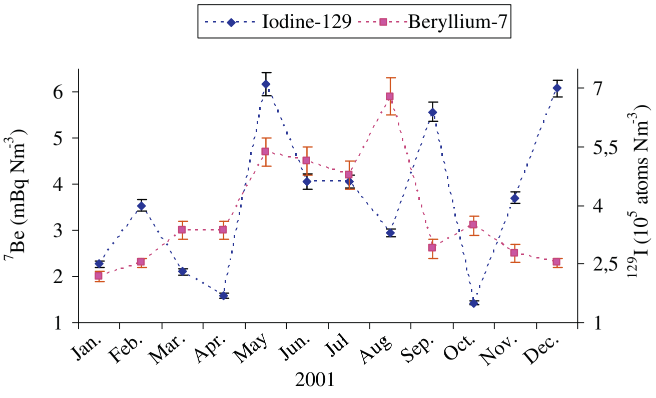

Fig. 6. Comparison of mean monthly concentration of ^{129}I and ^{7}Be.

4. Conclusions

- The results of this investigation reveal large annual variation in the concentration of ^{127}I, ^{129}I and ^{129}I/^{127}I isotopic ratios in air filters collected from Vienna, Austria.
- Significant temporal differences between iodine isotopes confirm different sources.
- The ^{129}I concentrations are strongly dominated by the gaseous emissions from the Sellafield reprocessing plant. The argument is supported by higher concentrations observed in May and September, consistent with higher emissions together with predominant winds from west and north-west at that time.
- The order of magnitude of the ^{129}I concentration levels are consistent with reported measurements in Sweden and Spain.
- Although ^{129}I and ^{7}Be show the same distribution pattern (higher values in summer and lower in winter), the opposite behavior observed in August and September reveal the different sources and may reflect predominant vertical and horizontal atmospheric mixing, respectively.
- The enhanced ^{7}Be concentration in summer is due to stratosphere-to-troposphere exchange and downward transfer on a large scale, which is also influenced by the meteorological parameters.

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